Nutrient Management Plans for NH Farms
Quality Assurance Project Plan

January 9, 2004

Prepared by
Tom Buob
UNH Cooperative Extension
3785 DCH, Box 8
North Haverhill, NH 03774

Project Manager:

<div style="text-align:right">
Signature / Date
Tom Buob, UNHCE
</div>

Project QA Officer:

<div style="text-align:right">
Signature / Date
Dr. Elizabeth Rochette, WA Dept. of Ecology
</div>

Program Quality Assurance Coordinator:

<div style="text-align:right">
Signature / Date
Andrea Donlon, NHDES
</div>

NHDES Quality Assurance Manager:

<div style="text-align:right">
Signature / Date
Vincent Perelli, NHDES
</div>

USEPA Project Manager:

<div style="text-align:right">
Signature / Date
Warren Howard, US EPA Region I
</div>

USEPA QA Manager:

<div style="text-align:right">
Signature / Date
TBD, US EPA Region I
</div>

A2 – Table of Contents

Appendices:

Appendix A: Standard Operating Procedures for Sample Collection and Lab Analysis
Appendix B: Standard Operating Procedures for Rainfall Simulation
Appendix C: Chain of Custody Form
Appendix D: Data Collection Sheet

List of Tables

List of Figures

A3 – Distribution List

Table 1 presents a list of people who will receive the approved QAPP, the QAPP revisions, and any amendments.

Table 1. QAPP Distribution List

QAPP Recipient Name	Project Role	Organization	Telephone number and Email address
Tom Buob	Project Director; Principal Investigator	UNH Cooperative Extension	603-787-6944 tom.buob@unh.edu
Dr. Beth Rochette	Project QA Officer; Co-PI	Washington Dept. of Ecology	509-736-3020 Broc461@ECY.WA.Gov
Amanda Gayda	Graduate Research Assistant	UNH Dept. of Nat. Res.	agayda@cisunix.unh.edu
Andrea Donlon	Program QA Coordinator	NHDES Watershed Management Bureau	603-271-8862 adonlon@des.state.nh.us
Vincent Perelli	NHDES Quality Assurance Manager	NH DES Planning Unit	603-271-8989 vperelli@des.state.nh.us
Warren Howard	USEPA Project Manager	USEPA New England	617-918-1587 Howard.Warren@epamail.epa.gov
TBD	USEPA Quality Assurance Officer	USEPA New England	TBD

Based on EPA-NE Worksheet #3

A4 – Project/Task Organization

Tom Buob, Extension Educator, University of New Hampshire Cooperative Extension (UNHCE), Dr. Elizabeth Rochette, former professor of Soil Chemistry, University of New Hampshire Department of Natural Resources (UNH Dept of NR) (currently with the Washington Dept. of Ecology), and Amanda Gayda (Graduate Research Assistant – UNH Dept of NR) are the principal individuals who are responsible for the research part of the nutrient management project. A description of each role is below.

Tom Buob – Project director and has overall responsibility for Task completion. Tom is responsible for supervision of graduate research assistant, oversite and direction on the identification of field research sites and collection of soils for indoor research efforts. He is the primary contact with NHDES and EPA, and will coordinate all project activities. (Since all sample collection is related to "simulated rainfall", there should be no need for "stop/go" instructions. Sample delivery will be arranged by the project director (since he will be directly involved in all simulations) to assure that the handling and sampling complies with the QAPP.) He will work with Dr. Rochette and Ms. Gayda in the interpretation and evaluation of the research data generated in this project.

Dr. Elizabeth Rochette – QA Manager and former academic advisor to Ms. Gayda. Dr. Rochette will review all data to assure that it meets the criteria spelled out in the QAPP and provide technical support in Soil Chemistry. She will also address all analytical problems related to analysis, and work directly with Buob and Ms. Gayda to resolve them.

Amanda Gayda - Graduate Research Assistant (RA) in the UNH Dept. of Natural Resources. Amanda is responsible for conducting the lab experiments related to this project, and will be conducting all of the chemical analysis of soil and water samples generated in the project. She will work with and under the direction of the Project Director (Tom Buob) to conduct the field and lab experiments. Amanda will

provide all data to Dr. Rochette for review and comment, and to determine that the data generated is appropriate to the QAPP of this project.

Figure 1 shows an organizational chart for this project.

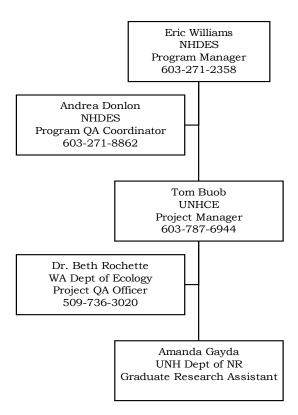**Figure 1. Project organizational chart**

Table 2. Personnel Responsibilities and Qualifications

Name and Affiliation	Responsibilities
Tom Buob, UNHCE	Project Director and principal investigator; see text above
Dr. Elizabeth Rochette, Washington Dept of Ecology, (former UNH professor of soil chemistry)	QA manager, see text above
Amanda Gayda, UNH Dept of Natural Resources	Graduate Research Assistant, see text above
Andrea Donlon NH DES Watershed Management Bureau	Reviews QAPP preparation and other QA/QC activities
Vincent Perelli NH DES Quality Assurance Manager	Responsible for review and approval of QAPP prior to EPA submittal
TBD EPA Region I Laboratory	Responsible for review and approval of QAPP

Based on EPA-NE Worksheet #6.

A5 – Problem Definition/Background

Background:

Phosphorus (P) is an essential nutrient for plant and animal growth, and its inputs have long been recognized as necessary to maintain profitable crop and animal enterprises. Historically, it has been understood that our soils have a high capacity to "bind" or hold P and make it unavailable to plant uptake. This has lead to the "misunderstanding" that New Hampshire soils have an infinite capacity to bind and hold P. Recent research, both in the northeast and New Hampshire (Buob and Rochette, 2003) has indicated that our various soils have different capacities to bind P, not only from crops, but also from runoff surface water and leaching to groundwater.

Phosphorus inputs can also increase the biological productivity of surface waters by accelerating eutrophication. While eutrophication is a natural aging of lakes or streams brought on by nutrient enrichment, it can be accelerated by human activities. In addition, eutrophication has been identified as the main cause of impaired surface water quality (U.S. EPA 1996).

Soil testing has been a very important tool in determining if and when there is a good probability of an increase in crop yield to added nutrients. This is the primary goal of any soil testing program. However, with an increased pressure to evaluate agriculture's role in non-point source pollution, some regulators thought that this would be a good method of determining if fields were contributing nutrients to surface water. A summary of New Hampshire soil test data (Buob. 2001) indicates that approximately 75% of soil test results for P are in the high or very high category. What this means from a soil testing perspective is that the probability of a yield increase to added P is minimal to none. What it does not mean (since soil testing is not designed for this purpose) is that these levels pose an environmental risk.

One of the goals of this project is to develop researched based guidelines to address the issues of nonpoint source pollution from agricultural lands. One approach now being used by a majority of states is the Phosphorus Site Index. This tool evaluates the sources of P at the field level, and the likelihood of

these sources to move to surface or groundwater. Unlike other states, New Hampshire does not have sufficient data on the relationships of our soils and the "threshold" soil test levels required for increased risk of offsite movement to occur. The data generated in this project will allow UNH Cooperative Extension (UNHCE) to develop the relationship between soil physical and chemical characteristics and the risk of increased P in runoff. Once these relationships are developed, they will be incorporated into UNHCE's nutrient management guidelines.

What questions need to be answered?

1. What is the relationship between soil test phosphorus levels (STP) and the concentration of dissolved reactive phosphorus (DRP) in the runoff for New Hampshire soils?

2. What physical or chemical soil characteristics have an effect on this relationship?

3. Are these relationships consistent or variable across our NH soils?

What will the data be used for?

The data generated from this project will be used to develop the best relationship between STP and DRP for a group of agricultural soils. Once these relationships are developed, we will design and evaluate management practices that will reduce the risk of P movement from these fields to surface water. These practices can then be incorporated into the nutrient management plans that are being developed for NH farms.

What decisions will be made with the project data and who are the principal users?

The data and conclusions from this project will be used to choose and/or adapt management practices that will reduce or minimize the risk of nutrient movement. These modified practices will be incorporated into the nutrient management plans that will be developed as part of the overall project. Therefore the principal users will be farmers, educators, state/federal agency and consultants who are involved in the development and/or implementation of nutrient management plans.

An example from some preliminary work (Buob et al., 2001) indicated that for a Marlow soil, as the STP increased above the Very High range (Soil Test P > 100 ppm) that the DRP in the runoff increased. Using the equation that defined the regression line, the DRP would exceed 1 mg/l when the STP approached 230 mg/kg (ppm). Previous work (Buob and Rochette, 2003) also indicated that the Marlow soils (Spodosol) had the highest P sorption capacity of all of the New Hampshire soils studied (25 soils) and that the P sorption capacities of the other soils (Entisols and Inceptisols) were lower. This indicated that the same STP level on different soils could have different environmental risk levels. One of the other characteristics that were noted to be of interest was the P saturation index. This is one of the chemical characteristics that will be investigated in this project to determine if it is more appropriate than STP.

A6 – Project/Task Description

Project: The goal of the project is to develop and implement nutrient management plans that minimize the risk of nutrient movement from agricultural fields into surface and groundwater. This will be accomplished by a series of tasks, most of which are not involved in the actual collection of environmental data covered by this QAPP. The Task related to this QAPP is listed here.

Task: Establish research and demonstration field sites on selected farms to determine relationships between STP levels and dissolved reactive P (DRP) in runoff from these plots; the effect of timing of manure application on DRP; and the effect of soil type on these relationships.

This task will be accomplished utilizing the rainfall simulation methods as prescribed by the National Phosphorus Research Project (NPRP- See Appendix B-12). This project is designed to develop valid relationships between a particular soil, the STP level measured in the soils lab (UNH Analytical Services Lab using a Mehlich 3 extraction) and the concentration of P in the runoff generated from the simulated rainfall. This data will then be analyzed and used to develop threshold STP levels, evaluate new management practices, or adapt current practices, to reduce the P concentration in the runoff as well as the risk of this runoff entering surface water. The project will involved conducting both indoor and field rainfall simulations in order to investigate a wide range of NH soils and soil characteristics.

Outdoor Rainfall Simulations:

The field objective of the outdoor rainfall simulations to be conducted is to characterize the STP – runoff P relationships for important agricultural soils across New Hampshire, and to evaluate the ability of various management practices to reduce the risk of movement of P to surface and groundwater.

Site selection – Site selection criteria includes soil type, soil test P level, soil test aluminum and iron levels (used to determine %P saturation), slope and current management. Initially the sites for outdoor rainfall simulations will be limited to the two selected demonstration farms (Briar Stone Farm, No. Haverhill and Stuart Farm, Stratham). These two farm locations present a diversity of soil types, ranging from glacial outwash to marine lacustrine soils.

Plot layout – Once sites are selected, plots will be established following the established protocol of the National Phosphorus Research Project (NPRP) (Refer to the diagrams at the end of Appendix B12). The surface runoff plots to be established consist of two (side-by-side) plots, each 1 m by 2 m, with the long axis orientated down slope. Soil slope is measured at each plot location. Metal borders are installed 5 cm above and below ground level to isolate surface runoff, which is diverted by a down slope gutter to a collection vessel. A representative surface soil sample (0-5 cm depth) is obtained after rainfall simulation by collecting 10 cores (2.5-cm dia.) from within each plot. Soil cores are air- dried and sieved (2 mm), and equal amounts are combined and thoroughly mixed to give a representative bulk soil sample for each plot.

Prior to each rainfall event, antecedent soil moisture is recorded using the TH2O Theta Soil Moisture probe. All information is recorded in a field log notebook. Simulated rainfall will be applied to each plot with one TeeJet^{TM} ½HH-SS50WSQ nozzle located in the center of a 305 by 305 cm aluminum frame about 245 cm above the plots. The nozzle and associated water piping, pressure gauge, and electrical wiring are mounted on the aluminum frame which is wrapped with plastic tarps to provide a windscreen. Local ground water and surface water is used as the water source for the simulator. The potential water sources for all simulations will always be analyzed for key constituents (P, Ca, K, Na, Cu, Zn, Al and Fe) prior to the simulations to ensure they are within acceptable and stated ranges as per the NPRP protocols. Finally, all water used to irrigate the plots will be sampled with each rain simulation. Since local water sources are utilized to produce the rainfall, duplicate samples are collected of the source water for analysis. If necessary, adjustments are made to account for any background P levels.

Water pressure at the rain simulator nozzle is regulated to 28 kPa to establish a water flow rate of 210 mL sec^{-1} at each nozzle. This pressure provides a coefficient of uniformity of ≥ 0.80 (80%) and produces "rain" drops with size, velocity, and impact angles approximating natural rainfall. A rainfall intensity of 7.0 cm hr^{-1} for 30 min is used. Surface runoff is collected in metal gutters at the down slope edge of each plot and pumped to 120 L (30 gallon) plastic containers. Total surface runoff collected is measured by weighing the containers, and a runoff sample is collected from the container after thorough mixing and agitation. A subsample of this runoff is immediately filtered (0.45 µm) and kept at 4°C, along with an unfiltered sample (reduced to pH of 2.0 then frozen) until P and sediment analyses are performed.

Dissolved reactive P (DRP), total dissolved P (TDP), total P (TP), dissolved organic P (DOP), and bioavailable P (BAP) concentrations will be determined for all surface runoff samples, using EPA Methods (see Table 9) – particulate P is estimated as the difference between total and total dissolved P. Throughout the scientific literature, DRP is sometimes referred to as dissolved orthophosphate or soluble reactive P (SRP). These terms all refer to the P fraction that passes through a 0.45-µm-pore-diameter membrane filter and responds to the molybdate colorimetric test without preliminary hydrolysis or oxidative digestion of the water sample. For purposes of consistency, this fraction will be referred to as DRP. Finally, for soil samples collected in each runoff event, Mehlich-3 P (STP), water extractable P (WEP) and bioavailable P (BAP) content will be determined (see Table 9). If the data is determined to be of value, soil samples will also be analyzed for total phosphorus (TP).

Indoor Rain Simulations:

The indoor soil box protocol has been established for specific conditions and objectives. First, when a site is extensively tilled to achieve plot uniformity, it is suggested that similar relationships between soil P and surface runoff P will be obtained with indoor runoff boxes as with field plots. However, it cannot be emphasized strongly enough that indoor boxes are not intended to replace field plots and are to be used in conjunction with field plots. The second scenario under which the indoor boxes may be used is to broaden the selection of soils evaluated. Clearly, the number of field plot sites that can be evaluated over the next two to four years will be limited. The indoor boxes will help strengthen the data base relating soil P and surface runoff P as a function of soil type.

Soil selection – Soil selection criteria include soil type, soil test P level, soil test aluminum and iron levels (used to determine %P saturation), slope and current management. Initially the soils for indoor rainfall simulations will be chosen to compliment the two selected demonstration farms (Briar Stone Farm, No. Haverhill and Stuart Farm, Stratham). While these two farm locations present a diversity of soil types, the indoor simulations allows for expanded selection to gather information on a wider range of NH soils.

Soil Collection - Soil from the surface (top 7.5 cm) of the selected sites is collected in a relatively dry condition with as little residue as possible. The sampled soil depth equates to the depth of soil used in the runoff boxes. The physical, chemical, and mineralogical properties are determined on each soil as per National P field protocol. Soils are air-dried in the laboratory, then sieved through a 19-mm sieve, and thoroughly mixed. Pretreatment of soil is minimal and a coarse sieve used to retain as much of the soil structure as possible.

Runoff Box Construction – Custom designed aluminum boxes (based on the NRDP protocol) 1-m long, 20-cm wide, and 7.5-cm deep soil boxes, with side and back walls 2.5 cm higher than the soil surface (See Figure 4a P Project Protocol Appendix B-12). The height of side wall is similar to the height of the field plot boundaries and should not result in any rain shadowing effect in boxes not in the center of the rainfall simulator. (Aluminum boxes are preferred over the wooden boxes due to their strength and durability).

Drainage holes (5-mm diameter) are located on the base of the box, at upper, mid, and lower locations. Although this will not replicate field drainage, some drainage is necessary and will improve reproducibility. Surface runoff is collected at the down slope end by a V-shaped aluminum trough. The shaped metal is overlapped and caulked to the outside lip of the box. A cover is attached to the end of the side-wall to protect the runoff collector trough from direct input of rainfall.

Packing the Box with Soil - The box is packed with a predetermined weight of soil, so that the final weight of soil in the box is known and the approximate bulk density of field soil can be achieved. Cheesecloth is placed on the bottom of box to cover the drainage holes, followed by the addition of 5 cm of soil. Soil is usually added several times to achieve the appropriate bulk density. We use a wooden

tamper to pack the soil during filling. Soil is added until it is level with the lower lip of the runoff box. After the desired bulk density is achieved by soil addition and tamping, the box is then placed at the required distance below the simulator nozzle (3.05m or 10 feet). Soils will be evaluated in triplicate, so that each soil should be packed into three different boxes for the runoff study.

Simulated Rainfall and Chemical Analyses - This portion of the protocol closely follows the field protocol discussed previously. Soils are pre-wet to control for antecedent moisture. A furnace filter is placed on the soil surface to protect the soil from raindrop impact, simulating crop cover. The soil is saturated using the rainfall simulator and the furnace filter removed. Saturated soils are left to drain for 24-36 hrs (covered with plastic) until field capacity is achieved. Volumetric soil moisture content is determined by theta probe. Runoff boxes can be set at two slopes, a field slope and a "common" slope (about 4 to 5%), with the field slope offering comparison with field data, and the common slope enabling comparison across the National P Project. At a minimum, soils should be evaluated under the common slope. Rainfall simulations are conducted three times, at one-day intervals between rainfall events to allow the soil to return to field capacity. Rainfall is applied at 7.0 cm hr-1 until 30 minutes of runoff has been collected (same protocol as for the National P field plots). A single bulk runoff sample (typically 5 to 7 L) is collected for the 30-min event. As per field protocol, discrete samples can be collected during the first few storms to define the P chemograph. Runoff volume, sediment yield, and P are measured as defined under the field protocol. Dissolved, bioavailable, and total P forms should be measured. Soil samples for chemical analysis should be collected from the material during packing. If samples are needed after a rainfall, a sample can be taken from the up-slope end of the box and replaced with a small amount of the original soil. As the boxes are prepacked, limited sampling at the upper end of the box will not affect flow pathways as in the field plots.

Table 3. Project Schedule Timeline

Activity	Dates (MM/DD/YYYY)		Product
	Anticipated Date(s) of Initiation	Anticipated Date(s) of Completion	
QAPP Preparation	09/01/2002	09/30/2003	QAPP Document
Site selection and establishment for outdoor rainfall simulations	09/1/2002	11/30/2003	
Identification and collection of soils for indoor rainfall simulations	09/1/2002	10/30/2004	Not applicable
Indoor rainfall simulations	07/15/2003	04/1/2005	Data on runoff P
Outdoor rainfall simulations	08/15/2003	10/30/2004	Data on runoff P
Data validation	Ongoing	03/01/2005	Data on runoff P
Data assessment report	Ongoing	03/01/2005	Data on runoff P
Final project report preparation		06/30/2005	Final Report

Based on EPA-NE Worksheet #10.

A7 – Quality Objectives and Criteria

The first step in the systematic planning approach for this project involved scoping, by determining research objectives based on the questions to be answered, existing data, types and numbers of samples needed to answer the research questions, sites (farms) available, and laboratory resources available. The second step involved determining the sampling and analysis plan and associated field and laboratory data quality objectives. The third step involved analysis of existing data as well as collection of new field and laboratory data; this process has been ongoing since the initiation of the project and will continue through year 2. Data quality assessment is concurrent with data collection, and involves inspecting performance

criteria for samples as data are generated. Additional data quality assessment will take place as data are prepared for publication, and will also be evaluated on the basis of comparison with the literature. As data are examined and interpreted, our goal will be to determine the appropriate approaches for examining site parameters for nutrient measurement and management. Table 4 summarizes the performance criteria for samples collected for this project.

Table 4. Measurement Performance Criteria for Surface Water Samples

Data Quality Indicators	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance
Precision-Overall	RPD < 20%	Field Duplicates
Precision-Lab	RPD < 35%	Lab duplicates
Accuracy/Bias	% Accuracy/Bias 85 - 115%	Spikes/Duplicates
Comparability	Deviation from SOPs should not influence more than 5% of the data	Data Comparability Check
Sensitivity	Not expected to be an issue for this project	Laboratory-fortified blanks at the QL
Data Completeness	90% samples collected	Data Completeness Check

Based on EPA-NE QAPP Workbook for 3/19/02 DES QAPP writing class.

Precision: Precision will be measured by analyzing sample duplicates and determining if they fall within the critical range for the specific protocol. If they fall within the critical range, the precision will be acceptable. If they fall outside the critical range, the samples will be analyzed again to determine if there were errors that lead to the imprecision.   Duplicate precision will be analyzed by calculating the relative percent difference (RPD) using the equation:

$$RPD = \frac{|x_1 - x_2|}{\frac{x_1 + x_2}{2}} \times 100\%$$

where x_1 is the original sample concentration
x_2 is the duplicate sample concentration

RPDs < 20% will be deemed acceptable

Accuracy/Bias. As an indicator of measurement confidence, percent accuracy will be calculated based on analytical results of spiked samples of known chemical concentration of phosphorus:

$$\% Accuracy / Bias = \frac{SpikedSampleConc. - UnspikedSampleConc.}{SpikedConc.Added} \times 100\%$$

Representativeness: Since we are trying to portray "true" but unknown systems (i.e., flow systems, soil test P: runoff P relationships and P related BMPs) through our research, it is important that the sites

and soils that are evaluated represent real situations in the field. The soils collected will represent a large portion of the agriculturally productive soils in the state, and the soil test levels and amounts of nutrients added will be representative of the current practices used by farmers. The plot selection process and design will insure that all of the rain falling on each of the plots will be channeled into the collection bottle for that plot. This will result in the runoff volume and P concentrations to be representative of the particular plot, soil type and soil test P level.

Comparability: Since the protocols and methods of analysis being used in this project (Appendix A) are the same as are being used in other states involved in the National Phosphorus Project, the data collected on our soils will be comparable to data developed in other states. To evaluate comparability of the data, we will continually examine the data being collected on this project in light of the data from other studies (published and in progress).

Sensitivity: Background soil and soil test P information on each proposed location exists, and the data show that the methods and instruments are able to detect the parameter of concern and other target compounds at the level of interest. If and when additional sites are identified, the background soil test data will be collected and analyzed to confirm that the methods and instruments are able to detect the parameter of concern. Detectable ranges of the methods and the equipment (found in Table 9 and the individual parameter SOPs) and the measurable range for individual parameters (Table 5) are adequate for the purposes of this study design.

Quantitation Limits. The analytical method, analytical/achievable method detection limit, and the analytical/achievable laboratory quantitation limits for this project are shown in Table 9 in Section B-4.

Completeness: Due to the nature of this project, we expect 100% completeness and this should not be an issue. During each rainfall event, there is a specific protocol (see Appendix B12) for generating runoff from the plots. If runoff is not generated after this specific period of time (2 hours), the simulated rainfall is halted for that run. If no runoff is generated on Day 2, then the simulation experiment is judged to be incomplete and no data is collected or recorded. Typically, runoff is generated prior to the time allowed (2 hours) and samples and data are collected. As long as runoff is generated, sufficient samples will be collected and the data set will be complete. Depending on whether a histograph or chemograph is desired, as few as 2 samples of collected runoff (one from each plot) can be used, since the objective is to compare the STP level to the DRP in the runoff collected from the plots.

Table 5. Soil and Water Sample Measurement Performance Criteria.

Matrix	Parameter	Meas. Range	Precision	Accuracy	Reporting Limit
Water	Diss. Reactive P, DRP	0.1 – 0.5 mg/L	10%	99%	0.02 mg/L
Water	Total diss. P, TDP	0.1 – 0.5 mg/L	10%	99%	0.02 mg/L
Water	Total P, TP	0.1 – 0.5 mg/L	10%	98%	0.02 mg/L
Water	Particulate P, PP	0.1 – 0.5 mg/L	10%	98%	0.02 mg/L
Water	Diss. organic P, DOP	0.1 – 0.5 mg/L	10%	98%	0.02 mg/L
Water	Bioavailable P, BAP	0.1 – 0.5 mg/L	10%	98%	0.02mg/L
Soil	Water extractable P	0.1 – 2.0 mg/kg	10%	N/A[1]	0.05 mg/kg
Soil	Mehlich 3-P	1 – 2400 mg/kg	10%	N/A[1]	5.0 mg/kg
Soil	Bioavailable P	0.1 – 0.5 mg/kg	10%	N/A[1]	0.05 mg/L
Soil	Total P	500 – 10,000 mg/kg	10%	N/A[1]	50 mg/kg

[1]Analytical accuracy not determined for soil due to a wide range in P adsorption-release characteristics

A8 – Special Training/Certification

Appropriate training of technicians, graduate students or other scientists associated with the specific tasks in the areas such as rainfall simulation techniques, soil collection and preparation, sample collection and chemical analysis will be the responsibility of the PI. Typically, all field sampling techniques and protocols follow generally accepted methodologies (see Appendix B-12). To date, the PI, co-PI and the Graduate Research Assistant have received training through Dr. Peter Kleinman and his staff (USDA-ARS) at the Pasture System and Watershed Management Research Unit Laboratory at University Park, PA. This training included 3 days for outdoor rainfall simulation techniques (site selection, site establishment, equipment calibration, sample collection and handling), 3 days for indoor rainfall simulation techniques (soil collection and preparation, experimental design, equipment calibration, sample collection and handling). The USDA-ARS laboratory staff also provided 1 day of training for the Graduate Research Asst. (Amanda Gayda) on the P analyses for soil and water samples.   Amanda, who has one year experience as an environmental chemist analyzing wastewater for various P fractions for a commercial lab, also received 4 hours training from the Analytical Services Lab Director in the use of the Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) equipment in the UNH Soils lab. Any additional training needs will be identified by the PI and provided by appropriate experts.

Table 6. Special Personnel Training Requirements

Project function	Description of Training	Training Provided by	Training Provided to	Location of Training Records
Rainfall Simulation	Outdoor and indoor preparation and techniques	USDA-ARS staff	Tom Buob, Amanda Gayda, Elizabeth Rochette	UNHCE-Grafton Co.
P Analysis	P analysis techniques and procedures	USDA-ARS staff	Amanda Gayda	UNHCE-Grafton Co.
Analyses	ICP Training	UNH ASL Director	Amanda Gayda	UNHCE-Grafton Co.

Based on EPA-NE Worksheet #7.

A9 – Documents and Records

Records and documents of data will be kept in both electronic and hard copy. A field notebook will also be used to make note of any conditions in the field that are noteworthy. For raw data collection, an example of the rainfall simulation data collection sheet is shown in Appendix D-14. The electronic form will be used to generate the hard copy form in order to facilitate data entry and the associated calculations. The electronic format to be used will be both spreadsheet and word processing documents (Excel, Word, Word Perfect, Quattro Pro).

Summary data will also be kept in both electronic and hard copy formats, using the software above. The PI, co-PI and Graduate Research Assistant (GRA) all have the same software packages (Microsoft Office) which was supplied by UNHCE. This same software will be used to summarize data and create the appropriate reports for DES and EPA personnel.

At the end of the project, the summarized data and report will be kept on file at the UNHCE-Grafton County Office in No. Haverhill for a minimum of 5 years. Results from this project will also be published as part of the Master's Degree thesis requirement and will be kept on file at the UNH library.

Other submissions to professional journals for publication will note the funding and support from
NHDES and EPA through Section 319 funds.

B1 – Sampling Process Design

For each outdoor rainfall simulation experimental site, there will be two side-by-side plots (1m x 2m)
on which the rain will fall and generate runoff. Prior to rainfall initiation, the antecedent moisture content
of the soil will be measured at 9 points in each plot using a Theta TH2O moisture probe (Dynamax, Inc).
Once runoff is generated, it will be collected at 5 minute intervals from the separate plots for a total of 30
minutes. The collected runoff will be weighed to determine volume and sampled to determine
concentration of the various P species of interest. (This can then be used to calculate a comparative
estimate of total load). For each site, runoff will be generated for at least 2 consecutive days, and the
procedure for sampling will be the same on each day. Each sample will be collected in new (1 qt) plastic
containers, capped and immediately stored on ice. A field duplicate will also be collected from each plot
on each day of the rainfall simulation event and handled the same as the regular samples. Duplicate
samples of the source water (rain) will be collected each day of rain simulation and handled the same as
the collected runoff samples. At the conclusion of the final day of rainfall simulation, soil samples of the
individual plots will be collected at two depths (0-5 cm and 0-15 cm) and analyzed for the various species
of P. Prior to analysis, the soil samples will be air dried and sieved using a 2mm soil sieve. Prior to
drying soil samples will be refrigerated at 4 degrees C. After analysis, the original soil and water samples
will be stored under refrigeration (4^OC) until the QA manager has reviewed the data from all the analyses.
If the data are deemed acceptable, the samples will then be disposed of. Water samples are poured down
the drain and soil samples are returned to approximately the same location from which they were
originally taken, if practical. Otherwise, they will be disposed of locally by spreading on an appropriate
landscape. For additional details, refer to Section A-6.

Table 7. Soil and Water Sample Summary (Outdoor Rainfall Simulation)

Parameter	No. of sampling locations	Samples per event per site	Number of sampling events	Number of field duplicates	Number of bottle blanks	Total number of analyses to lab
Water Samples						
Diss. Reactive P (DRP)	2	2	1 after 30 min	1/location-day 2 = 1	1/site = 1	6
Total diss P (TDP)	2	2	1 after 30 min	1/location-day 2 = 1	Not applicable	5
Total P (TP)	2	2	1 after 30 min	1/location-day 2 = 1	Not applicable	5
Particulate P (PP)	2	2	1 after 30 min	1/location-day 2 = 1	Not applicable	5
Diss. Organic P (DOP)	2	2	1 after 30 min	1/location-day 2 = 1	Not applicable	5
Bioavailable P (BAP)	2	2	1 after 30 min	1/location-day 2 = 1	Not applicable	5
Soil Extraction						
Water Extractable P	2	1	After simulation complete	Not applicable	Not applicable	2
Mehlich 3 P	2	1	After simulation complete	Not applicable	Not applicable	2

Parameter	No. of sampling locations	Samples per event per site	Number of sampling events	Number of field duplicates	Number of bottle blanks	Total number of analyses to lab
Bioavailable P	2	1	After simulation complete	Not applicable	Not applicable	2

Based on EPA-NE Worksheet #9c.

B2 – Sampling Methods

Sampling methods for soil and water are discussed in the SOPs (Appendix A-10 and A-). The sampling containers for runoff samples are new 1qt "food grade" plastic containers. Containers are used once, and new caps have also been purchased to eliminate any concern with contamination. Soil samples are collected using a standard stainless steel soil probe. The probe is cleaned between samples by wiping with a clean cloth or brushing to remove any residual soil. Soil samples will be air-dried and sieved (2mm soil sieve) within 48 hours of collection and stored dry in plastic soil sample collection bags at room temperature.

Failures in sampling methods are unlikely with soil samples since the equipment used to collect samples is very basic and unlikely to fail. Failures in collection of runoff will be evident from the quantities of water collected and from observation of the equipment during experiments by the operators. Experiments will be repeated as necessary to obtain reliable data. Decisions to repeat experiments will be made by the field personnel in consultation with the PIs. All experimental conditions, procedures, and events will be recorded in field notebooks. For additional details, refer to Section A-6.

Table 8. Sample Requirements

Analytical parameter	Collection method	Sampling SOP	Sample volume	Container size and type	Preservation requirements	Max. holding time (preparation and analysis)
Water Samples						
Diss. Reactive P (DRP)	Grab	Appendix A-5	250 mL	250 mL white polyethylene	H_2SO_4 to pH<2, light protected, chilled to 4ºC	48 hours
Total Diss. P (TDP)	Grab	A - 8	50 mL	500 mL white polyethylene	H_2SO_4 to pH<2, chilled to 4ºC	28 days
Total P (TP)	Grab	A - 7	250 mL	250 mL white polyethylene	H_2SO_4 to pH<2, chilled to 4ºC	60 days
Particulate P (PP)	Grab	TP – TDP *	100 mL	250 mL sterile white polyethylene	Chilled to ≤ 4ºC	48 hours
Diss. Organic P (DOP)	Grab	TDP– DRP *	NA	NA	NA	NA
Bioavailable P (BAP)	Grab	A - 6	100 mL	250 mL sterile white polyethylene	Chilled to ≤ 4ºC	48 hours
Soil Extractions						
Water Extractable P	Soil probe	A -1	200 g	250 mL clear whirl-pack	Air dried, sieved	None
Mehlich 3 P	Soil probe	A - 2	200 g	250 mL clear whirl-pack	Air dried, sieved	None

| Bioavailable P | Soil probe | A - 3 | 200 g | 250 mL clear whirl-pack | Air dried, sieved | None |
| Total P (TP) | Soil probe | A - 4 | 200 g | 250 mL clear whirl-pack | Air dried, sieved | None |

* These parameters are calculated from TP and TDP. Based on EPA-NE Worksheet #12b.

B3 – Sample Handling and Custody

Water samples will be collected by the person conducting the rainfall simulation (PI or Graduate Research Asst.) and brought to the lab on ice, and stored in a refrigerator at 4° C. The holding time for dissolved reactive P (DRP) is 48 hours (unpreserved), total P (preserved to pH < 2 with H_2SO_4) is 2 months.

Samples that are collected in the field or the lab are handled only by the original sampling personnel and subsequently, sample custody is consistent and straightforward. Likewise, chain-of-custody form (Appendix C) will accompany each batch of samples collected in the lab or field. These will indicate the total number of samples collected and shipped, the individual collecting the samples, and the lab to which the samples are being delivered. Soil samples will be collected using a standard Oakley soil sampling (tube) probe, will be air dried and sieved through a 2mm soil sieve (within 48 hours of collection) to remove stones and small debris. The samples will then be stored dry in standard plastic soil sample bags (whirl-packs) at room temperature ($25^{o}C$) until soil analysis can be performed.

After analyses, the original soil or water samples taken from the lab or field will be archived (water samples under refrigeration (4° C), soil samples at room temperature) until the appropriate researcher has had a chance to examine the data from the analytical lab. If the data are deemed acceptable, the samples will be disposed of. Water samples are simply dumped down the drain, while soil samples are returned to approximately the same location from which they were originally taken, if at all practical. Otherwise, they will be disposed of locally by spreading on an appropriate land use in an appropriate landscape.

B4 – Analytical Methods

All samples from field or laboratory experiments will be collected manually and transported to the analytical labs. There will be no analyses of samples by field instrumentation.

All water and soil samples will be analyzed by standard methods detailed in the **Standard Operating Procedures** for each method (see appropriate section of Appendix A for each analyte). In addition, all analyses from the laboratory will be checked by the laboratory manager to ensure correct dilutions, standard ranges, blind samples and blanks are being used, so that any suspect samples can be rerun. No samples will be analyzed out of concentration range, due to the non-linearity of the standard curve above a critical absorbance level. This critical absorbance level is set a conservative value of 0.800.

Standard EPA methods described in **"Chemical Analysis of Water and Wastes"** will be used for the analysis of all forms of P in water samples collected from surface runoff from experimental plots.

No EPA methods are available for soil P analyses as they relate to farm nutrient management and water quality impacts. Internationally recognized standard methods will be used with no modification of published protocols. These methods can be conducted by a wide range of laboratories with a high degree of reliability (Kleinman et al., 2001). In an inter-laboratory comparison of the soil P extraction methods used in this study, Kleinman et al. (2001) found a coefficient of variation of <10% for 24 soils from across the U.S., shared and independently analyzed by nine laboratories in AL, DE, FL, KS, MT, PA,

OK, OR, and WA. Clearly, the soil P extraction protocols to be used in this study yield data that may be reliably compared and compiled into watershed-scale data bases.

Analysis of soil samples will involve four standardized sample preparation/extraction techniques that yield different P components in soil as necessary to address research tasks. These methods are consistent with measurements required by farmers as part of the fertilizer and manure management recommendation process and for environmental risk assessment tools used in farm nutrient management planning. These risk assessment tools are used to delineate areas at greatest risk for P loss, identify appropriate BMPs, and target where these BMPs should be placed within the watershed. All original references for these methods are given in detail in <u>Methods of Phosphorus Analysis for Soil, Sediments, Residuals, and Waters (2000)</u>, and are summarized below. The P concentration of all soil extracts is determined by the colorimetric, two reagent method (**EPA Method 365.3)** (i.e., Murphy and Riley, 1962); a copy of the original reference is included as Appendix A-9. **Standard Operating Procedures** for all soil analyses are given in Appendix A. For additional reference, general P terminology used is defined in Haygarth and Sharpley (2000) and Sharpley (1993), included references.

Methods:

Water Analyses

- *Dissolved Reactive P* (DRP) of a filtered (0.45-µm) water sample is determined by the colorimetric, two reagent method **(EPA Method 365.3;** Appendix A-9**).**

- *Total dissolved P (TDP)* of a filtered (0.45-µm) water sample is determined by the Kjeldahl procedure using a block digester **(EPA Method 365.4)**. An appropriate water sample volume depending on P concentration (usually 5 to 20 mL) and 20 mL of water are digested with 1.133 gm of Kjeldahl reagent and 4 mL concentrated H_2SO_4. The mixture is digested, brought back to 25 mL, filtered through Whatman #1 paper, and P in the filtrate determined by the colorimetric, two reagent method **(EPA Method 365.3;** Appendix A-9**).**

- *Total P* (TP) is determined by the Kjeldahl procedure using a block digester **(EPA Method 365.4)**. An appropriate water sample volume depending on P concentration (usually 5 to 20 mL) and 20 mL of water are digested with 1.133 gm of Kjeldahl reagent and 4 mL concentrated H_2SO_4. The mixture is digested, brought back to 25 mL, filtered through Whatman #1 paper, and P in the filtrate determined by the colorimetric, two reagent method **(EPA Method 365.3;** Appendix A-9**).**

- *Particulate P (PP)* in water samples is calculated as the difference between total P and total dissolved P.

- *Dissolved organic P (DOP)* is calculated as the difference between total dissolved P and dissolved ortho-P.

- *Bioavailable P* (BAP) in water samples is determined using a technique developed by Sharpley (1993). One iron oxide strip is placed in 25 mL of sample and shaken for at least 16 hr. The iron oxide strip is then removed, rinsed with water, dried, and subject to extraction with 40 mL of 0.1 M H_2SO_4 for one hr. P concentration in the acid is then determined by the colorimetric, two reagent method **(EPA Method 365.3;** Appendix A-9**).**

Soil Analyses

- *Water extractable P* (WEP) in soil samples is determined by first shaking 2 g of the soil sample in 20 mL of distilled water for 1 hr (Appendix A-1). The supernatant is centrifuged and filtered through Whatman #1 paper, with P in the filtrate determined by the colorimetric, two reagent method **(EPA Method 365.3,** Appendix A-9**).**

- *Mehlich-3 P* (M3P) of soil is an agronomic-oriented extraction of P from a soil sample (Appendix A-2). This is determined by first shaking 2.5 g of soil in 25 mL of Mehlich-3 solution (0.2 N CH_3COOH + 0.25 N NH_4NO_3 + 0.015 N NH_4F + 0.013 N HNO_3 + 0.001 M EDTA) for 5 min. The supernatant is filtered through Whatman #1 paper, and P in the filtrate determined by the colorimetric, two reagent method **(EPA Method 365.3,** Appendix A-9**).**

- *Bioavailable P* (BAP) in soil is determined using a technique developed by Sharpley (1993; Appendix A-3). One gm of the soil sample is combined with 40 mL of 0.01 M $CaCl_2$ and one iron oxide strip, and shaken for at least 16 hr. The iron oxide strip is then removed, rinsed with water, dried, and subject to extraction with 40 mL of 0.1 M H_2SO_4 for one hr. P concentration in the acid is determined by the colorimetric, two reagent method **(EPA Method 365.3,** Appendix A-9**).**

- *Total P* (TP) for soil samples is determined by the Kjeldahl block digestion procedure **(EPA Method 365.4,** Appendix A-4**)** One g soil and 20 mL of water are digested with 1.133 gm of Kjeldahl reagent and 4 mL concentrated H_2SO_4. The mixture is digested, brought back to 25 mL, filtered through Whatman #1 paper, and P in the filtrate determined by the colorimetric, two reagent method **(EPA Method 365.3,** Appendix A-9**).**

Table 9. Soil and Water Sample Target Analyte and Reference Limits.

Phosphorus analyte	Method of analysis	EPA method	Detection limit	Duplicate precision	Accuracy
Water samples			mg/L	%	%
Diss. Reactive P, DRP	Colorimetric, two reagent	365.3	0.005	± 5	99%
Total diss. P, TDP	Kjeldahl digestion	365.4	0.010	± 10	98%
Total P, TP	Kjeldahl digestion	365.4	0.010	± 10	98%
Particulate P, PP	TP – TDP	365.3	0.010	± 10	98%
Diss. organic P, DOP	TDP – DP	365.3	0.010	± 10	98%
Bioavailable P, BAP	Fe-O strip and 25mL sample for 1 hour	N/A	0.010	± 5	98%
Soil extraction			mg/kg	mg/kg	
Water extractable P	Extract 2g soil and 20mL water for 1 hour	N/A	0.02	± 10	N/A[1]
Mehlich-P	Extract 1g soil and 10mL reagent for 15 min	N/A	0.02	± 10	N/A[1]
Bioavailable P	Fe-O strip and 1g soil for 16 hours	N/A	0.02	± 10	N/A[1]
Total P	Kjeldahl digestion	N/A	0.02	± 20	N/A[1]

[1]Analytical accuracy not determined for soil due to a wide range in P adsorption-release characteristics

After analysis, residual materials are disposed of as dictated by their acidity. Soil materials that have undergone water extraction or bioavailable P extraction (strip) are returned to their original field sampling location if practical. All other residuals are highly acidic in nature though, either because of the extractant used (Mehlich-3 extractant for soils, and H_2SO_4 extraction of the iron oxide strip for determining bioavailable P from water or soil), or the Murphy-Riley solution itself. These are disposed of according to University hazardous waste requirements.

Data will be compared to DQOs. When the required accuracy is not attained, the instrumentation will be recalibrated and any affected samples will be re-analyzed. These problems will be addressed by the analyst during analysis. When precision failures occur, the source of variability will be determined by comparing field duplicates and laboratory duplicates. Laboratory precision problems will be investigated and corrected by the analyst before analyses continue, and any affected samples will be re-analyzed. Field precision problems will be corrected by modifying collection techniques as necessary to reduce collection variability. Sample collection problems will be addressed by consultation between field personnel and the project PIs.

B5 – Quality Control

Table 9 summarizes the various analytical procedures that will be used in this project, including analytical method and detection limit. Quality control activities include running duplicates on approximately 5% of all samples, and use of laboratory quality control samples (standards) and analytical blank samples for every batch of samples run, typically in the range of 40 to 50 samples. Duplicate precision for dissolved reactive P and bioavailable P in water will not exceed 5% or samples will be rerun to determine an accurate value (Table 9). For digested and calculated values, the duplicate variability will not exceed 10%. In the case of low concentrations (i.e., <0.025 mg/L water P and <25 mg/kg soil P), duplicate precision will be relaxed to 10% for dissolved reactive P and bioavailable P and to 25% for the remaining analytes.

Reagents: Murphy Riley coloring reagents are prepared bi-monthly and stored at 4° C. Phosphorus stock standards and working standards are stored at 4° C and remade or re-purchased after holding time has expired (1 year for meat stock standards and vendor reported expiration date for other stock standards). 1+1 H_2SO_4 used for sample preservation is stored at 4°C. (Meat stock is a standard made directly from a solid, as in dissolving X g of KH_2PO_4 into reagent water for a specific concentration).

Table 10. Fixed Laboratory Analytical QC Sample Table

Analyte	Frequency of				
	laboratory duplicate	lab fortified matrix spike	lab fortified blank (QC standard)	lab reagent blank	independent calibration verification (QC standard)
DRP, TDP, TP,BAP (in water samples)	1 in 40	1 in 20	at beginning of tray after calibration and at end of run	at beginning of tray after calibration and at end of run	at beginning of tray after calibration and at end of run
WEP, M3 P, BAP and TP in soil samples	1 in 40	Does not apply	at beginning of tray after calibration and at end of run	at beginning of tray after calibration and at end of run	at beginning of tray after calibration and at end of run

Loosely based on EPA-NE Worksheet #24b.

B6 – Instrument/Equipment Testing, Inspection, Maintenance

The UNH Analytical Services Lab serves other projects than this one, and has lab-based instrumentation and maintenance protocols in place. Instrument testing is reflected in the laboratory quality control procedures (Appendix A) for the various procedures. The only maintenance to be

performed on the laboratory instruments is maintaining calibration and replacing flow cells and sensors as necessary.

All field-based equipment (runoff frames, runoff boxes, and rainfall simulator) will be inspected and tested based on the rainfall simulation protocol in Appendix B-12. Typically this is conducted prior to each rainfall simulation event. This same equipment will be inspected during routine site visits, or when problems with the data being collected suggest equipment malfunction. All problems encountered with data collection will be noted in data records, and if any of this data is used in reports or calculations, the problems will be included as part of the report. The ultimate appropriate use of any data will be determined through the review process with the QA manager and with researchers in other states using the same protocol (peer review).

Table 11. Instrument Equipment Maintenance, Testing, and Inspection

Equipment name	Activity	Frequency of activity	Acceptance criteria	Corrective action	Person responsible
Rainfall simulator	Maintenance (cleaning)	Monthly when in use	Free of soil particles	wash	Amanda Gayda or Tom Buob
	Calibration	Each Rain Event	Within 85% of desired flow rate	Adjust pressure	operator
	Inspection	Each Rain Event			operator
Runoff Frames	Maintenance (cleaning)	Monthly when in use	Free of soil particles	wash	Amanda Gayda or Tom Buob
Runoff Boxes	Maintenance (cleaning)	Monthly when in use	Free of soil particles	wash	Amanda Gayda or Tom Buob

Based on EPA-NE Worksheet #19.

B7 – Instrument/Equipment Calibration and Frequency

See above and refer to Appendix A (SOPs).

Table 12. Instrument/Equipment Calibration Table

Equipment name	Procedure	Frequency of calibration	Acceptance criteria	Corrective action	Person responsible
Rainfall simulator	Rainfall Intensity	Every rain event	Within 85% of desired flow rate	Adjust pressure	operator
	Rainfall Uniformity	initial	Coefficient of uniformity >/= 80%	Adjust to correct flow rate	operator
	Rainfall flow rate	Initial and beginning of each run	210 ml/sec	Adjust pressure	operator

Based on EPA-NE Worksheets #14 and 21.

B8 – Inspection/Acceptance Requirements for Supplies and Consumables

All supplies and consumables are purchased by the PI and inspected by the PI or the graduate research assistant. Items needed for lab analyses are purchased from chemical supply companies that the UNH has contracts with, for example, VWR and Thomas Scientific. Nonchemical items are shipped to the lab in

James Hall (UHN Natural Resources Dept) and inspected by Amanda Gayda on arrival. Chemical supplies must first be routed to the "Chemical Transfer Station" at UNH, logged in and then delivered to the appropriate room. Amanda Gayda inspects these as well.

Supplies and consumables needed for the indoor and outdoor rainfall simulation events are purchased by the PI and delivered to the PI at his office in Grafton County (North Haverhill, NH). After inspection by the PI, these are delivered to the appropriate location for use. To be acceptable, supplies must be delivered in closed packaging in good condition (hoses, clamps, fittings, etc). Lab supplies (including 0.45 um filters and syringes) are purchased as sterile and single use. Samples bottles and caps are purchased as sterile and single use, packaged in sealed plastic bags, and boxed for shipping.

Deionized water is obtained from a regulated source in the UNH Analytical Services Lab that consists of a Milli-Pore Filter System. Prior to use, glassware is acid washed in 15% HCl bath and rinsed 3 times in deionized water. Reagents: Murphy Riley coloring reagents are prepared bi-monthly and stored at 4° C. Phosphorus stock standards and working standards are stored at 4^oC and remade or rebought after holding time has expired (1 year for meat stock standards and vendor reported expiration date for other stock standards). 1+1 H_2SO_4 used for sample preservation is stored at 4^oC

B9 – Non-direct Measurements

This section is not necessary since we are not using data from outside sources.

B10 – Data Management

Raw field data is initially recorded on field record sheets and then transferred to a computer spreadsheet type program from which the field sheet was initially generated within 24 hours of the final rainfall event. The raw data is first reviewed in the field at the conclusion of each rainfall event to make sure that sufficient and appropriate data was recorded prior to leaving the site. Data review is repeated when the data is transferred onto the computer. This data is saved on the hard drive in spreadsheet form and backup copies are produced on either zip disk or compact disk (CD).

Laboratory data is initially hand recorded onto analyte-specific raw data templates as amount of sample used, dilution factors, and sample absorbance for colorimetric methods. Raw data is then transferred and stored to analyte specific templates in Microsoft Excel designed to calculate the total sample dilution factor, sample analyte concentration via sample absorbance, MS (Matrix Spike) percent recovery, CCV (Continuing Calibration Verification)/LCS (Laboratory Control Sample) percent recovery, and DUP RPD. Recording data directly onto raw data templates is double-checked during the recording process. Entering data from raw data templates into Microsoft Excel data templates is also double-checked. These data are saved on the computer hard drive as well as a backup copy on either zip disk or CD for review by the PI and QA manager. All participants in this project have access to spreadsheet type programs such as Excel.

ICP data is stored electronically directly into Microsoft Excel as a comma separated variable (csv) file and then converted to a spreadsheet (xls) file format. All file names and paths are incorporated into custom headers and footers so that printed copies (hard copies) have a location reference and date. This facilitates electronic storage and retrieval processes. Duplicate electronic copies are stored in a secured location for future reference in the event of a computer malfunction. Original raw data is also securely stored to avoid loss or destruction. Once sufficient data is generated, it is reviewed again by the PI, the QA manager and the research assistant. Statistical analysis includes (but is not limited to) ANOVA to determine "significant differences" between treatment, as well as regression analysis to determine how

strong the relationship (r^2) is between the soil test P levels and the DRP in the runoff. Initially this is conducted using statistical analysis available in the software package (Microsoft Excel, etc) with a more complete analysis to follow using more complicated statistical packages such as SAS or SYSTAT.

C1 – Assessments and Response Actions

Assessments of each field runoff event will be made as to the functioning accuracy of the equipment at the time of individual rain events. Since the factors affecting the data generation process are in the control of the persons (PI and/or RA) conducting the experiment, steps will be taken prior to data generation to assess any data quality issues. If an assessment identifies a data quality issue, the appropriate response actions (calibration, pressure adjustments, etc) will be made prior to data generation and collection. Refer to Section B7, Table12, Equipment Calibration.

The equipment operator (PI or RA) have complete authority to determine if the data generation process will meet the required criteria for the specific project objective. If it does not meet the required specifications, data will not be generated or recorded at the site and the experiment will be cancelled.

During the generation of laboratory data, ongoing assessments will be made with respect to the functioning of the lab equipment and to the appropriateness of the data. If an assessment determines that there has been inappropriate data generated, that data will not be used and the analysis will be redone. The appropriateness of the data will be based on the performance criteria set out in Table 1. The assessment will be conducted by the person conducting the analysis (PI or RA) and then reviewed by the QA manager at the appropriate time. The result of all assessments that require any response actions will be recorded in both the field notebook for the field studies and the lab notebook for any laboratory assessment/response actions. These will be initialed by the person(s) making the assessment and the resulting response.

Table 13. Project Assessment Table

Assessment Type	Frequency	Person responsible for performing assessment	Person responsible for responding to assessment findings	Person responsible for monitoring effectiveness of corrective actions
Field sampling audit	Once at beginning of each rainfall event	Operator (PI or RA)	Operator (PI or RA)	Operator (PI or RA)
Lab analytical assessment	Weekly	Amanda Gayda	Amanda Gayda	Amanda Gayda

Based on EPA-NE Worksheet #27b.

C2 – Reports to Management

Report on progress, and the status of the Tasks will be submitted to NHDES at least once every six months by the PI (Tom Buob). A final project report will be submitted to DES at the completion of the contract which expires on June 30, 2005. In addition, data summary reports will be reviewed and discussed with the QA manager on a regular schedule (at least once per month) to assure that any QA issues are addressed in a timely fashion.

Once each year, the QAPP will be reviewed by the PI (UNHCE) and the QA manager to determine if any revisions are required. A letter documenting this review will be filed with the appropriate approval authority, and copies will be sent to the recipients and organizations on the QAPP distribution list (Table 1). If only minor revisions are needed that do not require approval, the letter will document all revisions to the QAPP. If revisions are made that do require re-approval, then these revisions will be submitted in a letter form for approval, or if significant changes are required, a revised QAPP document will be submitted for review and re-approval.

D1 – Data Review, Verification and Validation

The emphasis for this project will be to perform data review as soon as possible after data are collected, so that samples can be re-analyzed as necessary within holding times, and field errors can be corrected as soon as possible. Since it requires a minimum of 2 people to do a rainfall simulation event, the field data will be reviewed at least twice prior to being entered into an electronic form, and then a third time when it is entered. Any unusual circumstances in the field will be noted and recorded in the field notebook, and all field notes will be attached to raw, validated, and verified data so that field conditions are always evident during data interpretation. This will also allow transcription errors to be caught and corrected by the field personnel or analyst during data collection. In the lab, some analytical data collection will be automated by the instrumentation, thereby preventing transcription errors in these cases. However, most data *is* initially hand recorded onto analyte specific raw data templates. This allows for a review as the data is being recorded as well as when it is entered into the electronic form (Refer to Section B-10). If there is any indication during this transcription and review process that the data is not appropriate or accurate, the data will be flagged for an additional review and assessment by the QA manager and the PI.

Data verification will involve comparison of quality control samples with the parameters in Table 5 by laboratory personnel, the QA manager and the PI. The same parameters will be used for data validation. Samples will be re-analyzed whenever possible (when holding times and sample quantities allow). All data collected outside of holding times will be flagged with an explanation regarding the time of analysis. All samples associated with failures of quality control parameters will be rejected, and re-analyses will take place if possible. The analyst will flag data, re-analyze samples based on quality control criteria, and flag any data that violates the Table 5criteria. The PIs will decide if the data will be rejected or accepted, based on the nature of the violation (rejection will generally be the rule).

Samples exceeding the calibration concentration will be diluted and flagged to indicate that dilution was needed. Values below the PQL will be reported with a flag of "BPQL" (below practical quantifation limit), though they will be used in calculations unless the values are less than half of the PQL; values less than half the PQL will be assigned a value of zero and given a flag of BPQL. Missing data will be flagged as NA (for not available), and will not be used in calculations. No estimated values will be reported or used in calculations.

D2 – Verification and Validation Procedures

As mentioned in section D1, non-conformities in quality control parameters will be kept to a minimum by re-analysis as necessary. Holding time violations or other quality control violations will be indicated in data spreadsheets in a Comments column.

A second level of validation will involve considering expected ranges for the samples, and statistical analyses examining confidence limits for normal and lognormal distributions of the data. Samples

outside 95% confidence limits will be examined in detail, considering all associated flags and field notes. In some cases, reanalysis will take place to assure that the original values are correct, with the underlying assumption being that original values were correct and the "outliers" are an artifact of natural field variability. Apparent "outliers" will be flagged to indicate that they are outside the 95% confidence limit, and any associated re-analyses will be indicated in the data spreadsheet in the Comments section.

D3 – Reconciliation with User Requirements

The objective of this project is to generate data that can be used to develop relationships between soil properties and the amount of P in runoff. To accomplish this, various studies will be conducted to relate the STP (soil test P) to the DRP in the runoff. These relationships will also be evaluated (statistical analysis, etc) with respect to the various soil properties of the various soils used in the study.

A review of data will involve graphs of expected relationships between variables to address hypotheses. For example, Buob and Rochette (2003) have shown a relationship between phosphorus saturation indices and soil sorption maxima for phosphorus. This relationship is expected to hold in this study; therefore, comparisons will be made between concentrations of extractable P and (aluminum + iron), and between measured soil P sorption maxima and the ratio of extractable (P/ (aluminum + iron)). This will provide an additional opportunity to examine confidence limits and look for "outliers", though, again, the data will be assumed to be valid unless they can otherwise be shown not to be valid. In addition to examining statistical relationships, processes creating the relationships will be considered, and management adjustments will be suggested to offset or utilize important natural processes at the sites examined and similar farms to prevent nutrients from reaching surface or groundwater.

As these relationships are being developed, we will also be evaluating the data to determine if there is a reasonable way to consolidate soil types (based on specific properties) into management groups. If this is possible, P based management practices can be based on soil groupings (similar physical and chemical properties) rather than on individual soils. This would facilitate the development and implementation of management practices more quickly than if individual soil types were used. This would also make the farmers' approach more reasonable, and therefore, more likely to be adopted.

References

Buob,T.E. (2000). Sabbatical Leave Report. The State of Nutrient Management in New Hampshire. UNH Cooperative Extension, Durham, NH

Buob,T.E, P.A.Kleinman, A.N. Sharpley and E.A.Rochette (2001). National Phosphorus Runoff Project: New Hampshire. http://pswmru.arsup.psu.edu/phosphorus/ProgressReports/NewHampshire.pdf

Buob,T.E. and E.A. Rochette, 2003. Status of Phosphorus in Soils of the Connecticut River Watershed in New Hampshire. Communications in Soil Science and Plant Analysis. Vol. 34, Nos. 7&8, pp. 1177-1192.

Haygarth, P.M. and A.N. Sharpley. 2000. Terminology for Phosphorus Transfer. Journal of Environmental Quality 29:10-15.

Kleinman, P.J., A.N. Sharpley, K. Gartley, W.M. Jarrell, S. Kuo, R.G. Menon, R. Myers, K.R. Reddy, and E.O. Skogley, 2001. Interlaboratory comparison of soil phosphorus extraction methods. Communications in Soil Science and Plant Analysis. 32:2325-2345.

Murphy,J. and J.P.Riley. 1962. A modified single solution method for determination of phosphate in natural waters. Anal. Chim. Acta 27:31-36.

Pierzynski, G.(ed.) 2000. Methods of Phosphorus Analyses for Soils, Sediments, Residuals, and Waters. SERA-IEG 17 Regional Publication No. 396. http://www.soil.ncsu.edu/sera17/publications/sera17-2/pm_cover.htm

Sharpley, A.N. 1993. Assessing phosphorus bioavailability in agricultural soils and runoff. Fertilizer Research 36:259-272.
U.S. Environmental Protection Agency. 1994. Water quality standards handbook. 2nd Edition. Office of Water, U.S. Environmental Agency, Washington, DC. EPA 823-B-94-005a.

U.S. Environmental Protection Agency. 1996. Environmental indicators of water quality in the United States. EPA 841-R-96-002.